METHODS AND RESULTS OF OZONE MEASUREMENTS OVER MOUNT EVANS, COLO.

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This paper gives data on the total amount of ozone above Mount Evans, Colo., during the latter part of July 1936 and 1938, as determined from ultraviolet measurements by a photoelectric cell and filter method. The method, especially the calibration of the photoelectric cells, is discussed in detail. The measurements indicate ozone in the stratosphere in the amount of 0.20 to 0.22 cm. normal temperature and pressure, which is in good agreement with determinations by others for the same latitude and season of the year.

Incidental to the work, a new determination of the solar energy curve in the short ultraviolet wavelengths outside the earth's atmosphere is made.

I. INTRODUCTION

The usual method employed in the study of the total amount of ozone above a given point has been that of measuring the intensity of the solar radiation at one or more wavelengths within the ozone absorption band, that is below 3200 angstroms, relative to some longer wavelength or wave lengths outside the region of ozone absorption. Ordinarily a photographic method is utilized; and measurements are made at two or more different air masses (air mass equals approximately the secant of the sun's zenith distance) and upon the assumption that both the ozone content and solar emission remain constant during the interval.

It is doubtful if either the ozone or the solar energy remains constant for a very long period; and both are thought to change in cycles, the ozone with the season (**1**) and the solar emission with the sunspot cycle. Short periods of variation of the order of days and hours have been noted by others and also appear in the results of our own work at Mount Evans, where there was observed a definite variation in the filter transmissions, indicating a variation in either (or both) the ozone content or the spectral quality of solar emission in the ozone band. It would be very difficult to separate the two effects, and it is questionable if any of the present methods are sufficiently sensitive to accomplish this result. However, the effect of any change in solar emission within the range of wave lengths reaching the earth's surface, even upon a mountain top, is much less than that of the ozone, and for the present may be neglected without making a serious error in the determination of the ozone.

It has been recognized by others (e. g. by Götz who made some filter measurements), and was pointed out in connection with the report on some stratosphere measurements (**2**) at the National Bureau of Standards in 1937, that it should be possible to follow the ozone cycle through the year and from year to year by means of photoelectric cell and filter measurements. However, owing to certain difficulties, especially the lack of time to work out sufficiently accurate methods for the calibration of the spectral response of the photoelectric cells, no definite progress along these lines was made until recently (**12**), when a preliminary report on this work was prepared and given before the April 1939 meeting of the Meteorological Section of the American Geophysical Union in Washington, D. C. It is a relatively simple matter to get qualitative measurements of ozone variation by this method, but accurate quantitative values require a careful evaluation of the photoelectric response, especially in the longer wave lengths to which the cell responds. These wave lengths, owing to their higher intensity in sunlight, produce a large part of the total photoelectric response of the cell.

Furthermore, the conditions at Washington, D. C., low altitude and high humidity, militate against the study of the amount of ozone in the stratosphere from a ground station because of variations of atmospheric transmissions in the lower levels of the atsmosphere, below 10,000 feet, caused by dust, smoke, etc. Measurements at high altitude minimize errors that are inevitable through the more vitiated lower atmosphere; hence, the present report deals only with measurements on Mount Evans above 10,000 feet in elevation in 1936 and 1938.

Unfortunately, neither the observing period in July 1936, nor in July 1938, comprised many clear days. In 1936, when the measurements were made by the senior author at Echo Lake (altitude 10,600 feet, on the north slope of Mount Evans) only 1 of the 10 days spent there remained practically cloudless throughout the day. On 4 other days measurements were obtained during part or all the morning. The afternoons were cloudy and there was usually rain, and on 3 days sleet and snow in the late afternoon. A view of Echo Lake is shown in figure 10.

On the peak of Mount Evans (altitude 14,260 feet) in July 1938, when the measurements were made by the junior author, high clouds or broken cumuli prevailed during the morning hours. On 8 of the 9 days spent at the crest, the cloudiness increased shortly after noon, on some days with great rapidity, and on all 8 days was followed by rain, hail, sleet, and snow; generally in the order named. We were fortunate, however, in having less trouble from static than had been anticipated; we had prepared for possible difficulties by observing with both our instrumental equipment and bodies well grounded by copper wire to avoid undesired fluctuations of the current in the measuring instrument. At times the potential gradient is so strong on Mount Evans that not only is the reading of electrical equipment impracticable, but the observer has to take advantage of the copper-roofed and copper-sided observatory to avoid uncomfortable sparking from his body to the ground. Views of Mount Evans and the observatory are shown in figures 12 and 13.

The method herein described of obtaining the amount of ozone in the stratosphere makes use of titanium photoelectric cells and filters as described in the paper by Coblentz and Stair (**3**) on studies of ultraviolet solar intensities. For this work, however, as noted above, a much more elaborate calibration of the photoelectric cell for spectral response and of the filters for spectral transmission is required than was used in the preliminary study of total solar ultraviolet intensities.

Since the major part of the work of a research of this type consists of an accurate determination of the spectral response of the photoelectric cells, the transmissions of the filters and the mathematical evaluation of the data, and since the method is a modification of that employed in the determination of the distribution of ozone in the stratosphere (**2**), a considerable portion of this paper is given to a discussion of the general method, especially the spectral calibration of the photoelectric cells.

Suggestions concerning improvements in certain phases of this type of work, especially in the method of obtaining

the data are given where avoidance of mistakes is especially helpful.

II. THE PHOTOELECTRIC CELLS AND FILTERS

In this work four titanium photoelectric cells [1] and four filters (Corex D; Nillite; Barium Flint, 1 mm.; and Barium Flint, 3 mm.) having the spectral responses and transmissions depicted in figure 1 were employed. Cells Nos. 2 and 6 were used in 1936 and Nos. J–4 and D–6 in 1938. Two sets of filters, alike in ultraviolet spectral transmission were employed in this work; and several tests, before and after their use, established their constancy and agreement in transmission. The same filters were used also in the photo-electric calibrations with the Mazda CX lamp, described in section 2. Their transmissions

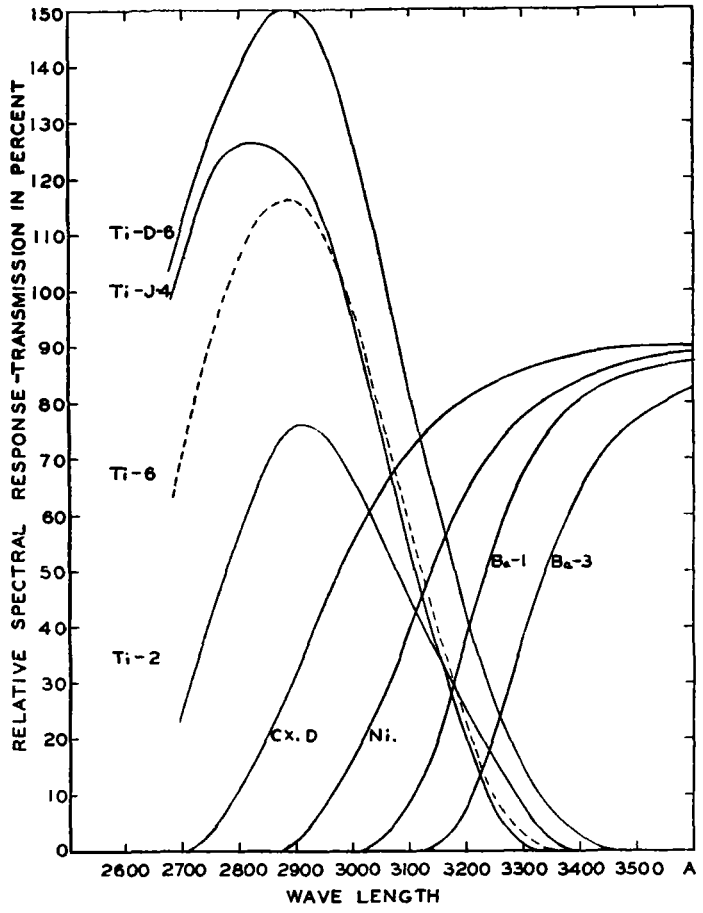

FIGURE 1.—Graphs showing the relative spectral response curves for the four titanium photoelectric cells; also the spectral transmissions of the filters.

were determined at the wave lengths of the mercury emission lines and the shapes of the curves between points adjusted for best agreement with calculations on other thicknesses of glass and integrated transmission magnitudes as calculated from their use with the Mazda CX lamp. Consequently, any errors will be partly balanced out by the fact that the Mazda CX lamp has a spectral energy emission curve in the ultraviolet spectrum somewhat similar in shape to that of sunlight. (See figure 2.)

1. *Spectroradiometer calibration of the photoelectric cells.*—The spectral response of the photoelectric cells was obtained by two supplementary methods; the first of these being the commonly employed, spectroradiometric method, in which the strong emission lines of a mercury arc lamp and a cadmium arc lamp are used to obtain an equal energy response at the wave lengths of the emission lines. In this calibration the same slit defined the energy for the photoelectric cell and for the thermopile, the two being moved alternately behind the slit. In the spectral calibration of photoelectric cells by this method, the irradiated portion of the cell shifts slightly with wave length because of variation in focus and angle of emergence of the radiation; so that as the result of unequal sensitivity, or shadowing by the central electrode within the cell, erroneous values may result. Several measurements with different adjustments of the cells, however, partly neutralized these effects.

This method of calibration is consequently not sufficient, especially for wave lengths longer than 3,200 angstroms, which is close to the wavelength limit of sensitivity of the cell. It was especially difficult to define the response between the wavelengths 3,261 and 3,404 A. (cadmium arc lamp emission lines) for the titanium cells used in this study. A slight variation in the curvature of the response curve between these points produces a marked effect upon the total integrated transmission values of the

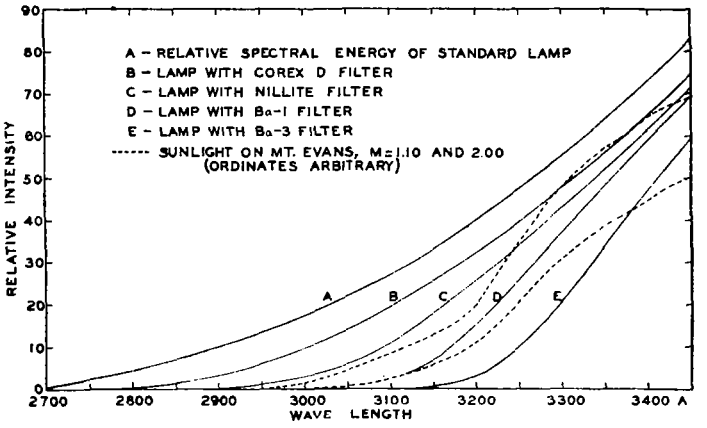

FIGURE 2.—Graphs showing relative spectral energy curves of the standard lamp and of the sun. The curves for the lamp are greatly magnified relative to those for the sun.

filters. Since the response at 3,404 A. was of the order of one-thousandth, or less, of that at 2,967 angstroms for some of the cells, extreme caution was necessary in the use of exclusion and transmission filters with the spectrometer to insure freedom from stray light of other wave lengths. For this reason measurements made upon the weak mercury line at 3,340 angstroms were not satisfactory. In solar radiation, these wave lengths produce a large effect upon the total response of the cells and upon the total transmission of the filters; hence the great importance of knowing accurately the spectral response in this region. For this purpose a supplementary method of calibrating the photoelectric cells is employed.

2. *A source of continuous spectral ultraviolet radiation for calibrating photoelectric cells.*—Toward this end a standard of continuous ultraviolet radiation in the form of a Mazda CX lamp was set up. The approximate shape of the emission curve in the ultraviolet was known from data by W. E. Forsythe (**10**) on the Mazda CX type of lamp operated on 115 volts. Since this standard was a particular lamp and was operated on a slightly lower voltage (110 volts to insure longer life) these general data could not be directly applied.

By trial and error, corrections to the general emission curve [2] in the short wavelength region were calculated

[1] Westinghouse type WL-767 titanium photo-electric cells were used in this work.

[2] If a suitable black body, or even a filament lamp of known spectral emission, had been available this part of the work would have been greatly simplified.

FIGURE 10.—Echo Lake, elevation, 10,600 feet.

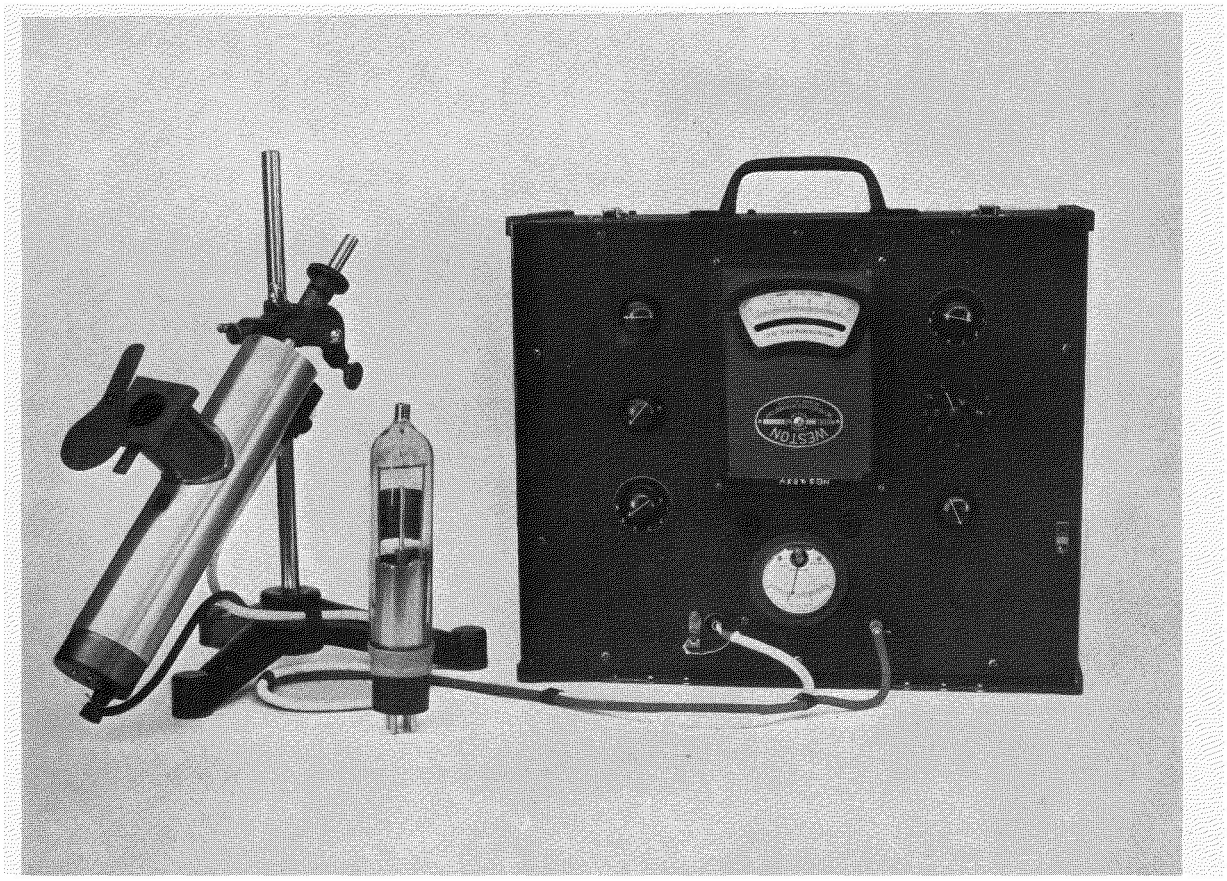

FIGURE 11.—Ultraviolet meter, titanium photoelectric cell, and cell mounting.

FIGURE 12.—Cumulus cloud over Mount Evans Observatory, elevation, 14,260 feet.

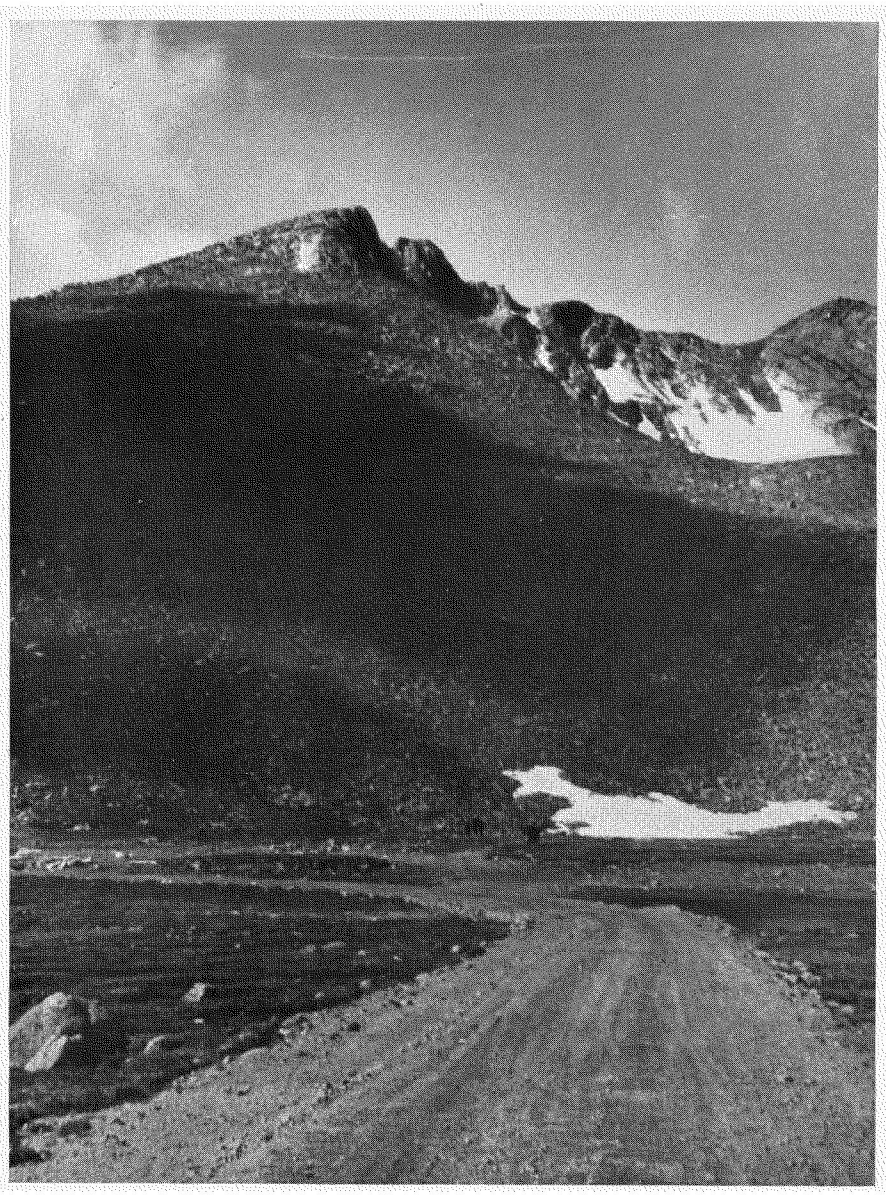

FIGURE 13.—Mount Evans peak from Summit Lake, elevation, 14,260 feet.

from the filter transmissions (the same four filters as employed in the solar measurements) using the average for eight titanium photoelectric cells which had been carefully calibrated by the spectroradiometric method and were known to have a relatively sharp cut-off at the longer wave lengths. Hence, since the shape of the lamp emission curve was already fairly well known in the longer wave lengths in the ultraviolet (above 3,100 A.) and since the photoelectric cell response curves were known quite accurately below 3,150 A. the spectral energy curve in the short wave-length region obtained by this method is, no doubt, better than could be measured directly with a spectroradiometer.

The Mazda CX lamp approximates sufficiently close for our work the solar emission in that portion of the short ultraviolet spectrum to which the photoelectric cells are sensitive, having, as does the sun, a high emission in the region where the photoelectric cells have a low response. By measuring a set of integrated transmissions of a group of calibrated filters with this lamp as a source, and by calculating the integrated transmissions of the same filters from a knowledge of their spectral transmission, the spectral energy emission of the lamp, and the spectral response of the photoelectric cell (based upon an arbitrary curve drawn through the values for the wavelengths at which the response was determined spectroradiometrically) the shape of the photoelectric cell response curve, especially between 3,261 and 3,404 angstroms and for longer wave lengths, was altered until the observed and calculated transmissions were in agreement. In this manner the shape of the spectral photoelectric response in the region of 3,200 to 3,400 A. was obtained.

In addition, for some of the cells, the apparent emission curve of the lamp was altered, by covering the photoelectric cell permanently with one of the filters, and the process repeated. That gave a new standard of continuous ultraviolet radiation with the energy curve shifted toward the longer wave lengths (see fg. 2). Since the Mazda CX lamp as used (a 500-watt, 115-volt lamp operated on 110 volts) was richer in short ultraviolet relative to longer ultraviolet wave lengths than sunlight, this modification gave filter transmissions, and hence an energy curve, approaching closer to sunlight in the spectral range 3,000 to 3,300 angstrom units. The spectral response values of the photoelectric cell were again altered, if necessary, for best agreement between the calculated and observed transmissions.

In this second method of calibration of the response of the photoelectric cell no trouble is encountered with scattered light and the cell is tested, as used in practice; that is the cell is fully and evenly irradiated.

The Mazda CX lamp method appears to be a very satisfactory means of determining the existence and magnitude of the long wavelength "tail" of the photoelectric cell response curve. For cells of certain types (not the titanium cells as used in the present work) 50 percent or more of the total response in sunlight may be due to long wave lengths at which the relative response is less than 1 percent of the maximum value and would not be detected at all, or, at best, inaccurately determined even with the most careful work by the spectroradiometer method. Although the spectral response in the long wave lengths may be only a few parts in a thousand, relative to that at the maximum for the cell, the total integrated filter transmissions may be affected by amounts which in practice would give calculated values of ozone in error by a factor of two or more.[3]

[3] A cell having an extremely broad long wavelength response should not be used in ozone determination work because of the difficulties encountered in evaluating the data when the response covers so long a spectral range.

This method of calibration of the spectral response of a photoelectric cell may be extended to include filters of both longer and shorter wave lengths cut-off, for use with other types of cells. It is of course not recommended as a sole means of obtaining response curves, but will give an approximate curve without a great amount of calculation if the approximate location of the maximum response and the general type of the response curve are known.

By measuring the filter transmissions from time to time, using the Mazda CX lamp as a source, the constancy of the relative spectral response of the photoelectric cells is checked. Although no filter measurements on our four cells had been made before the observations on Mount Evans, check measurements during the past year indicate that these cells have undergone no measurable change. Furthermore, solar observations obtained at Washington, before and since the Mount Evans work, are in agreement. Check measurements on photoelectric cells which have been used but little in the meantime also indicate that the relative spectral emission of the Mazda CX lamp has undergone no measurable change over a total operating period of

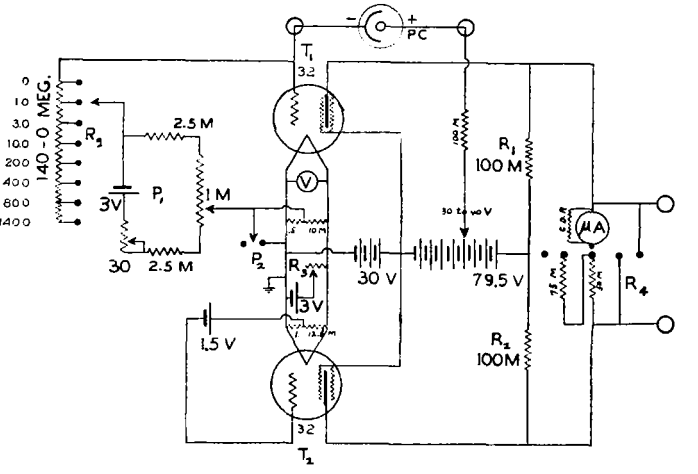

FIGURE 3.—Electrical circuit of the ultraviolet meter.

about 30 hours. Since the lamp is operated on a fixed voltage (instead of amperage) below the normal working value only a very slow change is to be expected.

III. THE ULTRAVIOLET METER

A portable ultraviolet meter in which the photoelectric current is amplified and then measured by a microammeter was easily transported to the mountain stations. Two of these instruments, designed by one of the authors in collaboration with W. W. Coblentz at the National Bureau of Standards, and now obtainable from the Bendix Radio Corporation of Baltimore, Md., were used in the present work. The instrument, an original model (4) of which has been described previously, is shown photographically in figure 11 and diagrammatically in figure 3.

Briefly described, this instrument is a balanced direct-current amplifier built in the form of a Wheatstone bridge.[4] A condition of unbalance results when light falls upon the photoelectric cell producing a flow of current through a microammeter proportional to the intensity of the radiant energy incident upon the cell. Practically

[4] In reference (4) earlier arrangements of amplifier circuits involving the Wheatstone bridge principle are cited.

all the component parts are standard radio materials. All the resistors and potentiometers, except those in the grid circuit, Rg, are of the wire wound precision type. S. S. White Dental Manufacturing Co., type 65X, resistors have been found to be suitable for the grid circuit units. In the assembly all units are carefully soldered and moving elements having pressure contacts on the shafts are provided with soldered "jumpers" supplementing the pressure contacts. Even the grid batteries and tube electrodes are connected into the circuit with soldered leads.

The resistors, Rg, are mounted on hard rubber or bakelite and all connecting wires are air insulated. The photoelectric cell connecting cable is doubly insulated with rubber, ordinary rubber covered wires being pulled within a piece of chemical rubber tubing of high quality and the grid lead electrically shielded. Leakages within the cable, or photoelectric cell mounting case, are readily located by means of the deflection observed with the

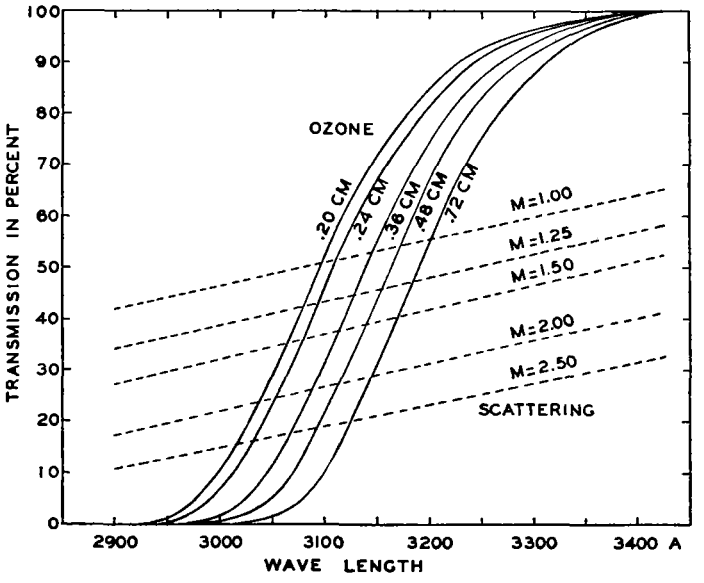

FIGURE 4.—Graphs showing the spectral transmission of the atmosphere in terms of molecular (Rayleigh) scattering and ozone absorption.

leads alternately connected and disconnected from the amplifier.[5]

Although, not used in the present work, the instrument should contain a drying pack, especially when used in a mountain location where wide changes in temperature and humidity occur. Errors produced by moisture on the resistors and mountings of the instrument may affect the total intensity measurements seriously but not the percent transmissions upon which our ozone calculations are based. Some of the variations observed in total intensity may thus be partly instrumental error.

In performance, three instruments tested over a wide range in intensity showed a linear response to within about 1 percent. This precision is about the maximum that can be expected with electronic apparatus in which the radio tube characteristics enter in a direct way. Since the microammeter deflection was kept near the same scale value, by adjusting the sensitivity of the amplifier, the precision probably remained within 1 percent during most of the work.

With poorly balanced tubes, or tubes with high grid current characteristics, or with improper bias or plate voltages, errors in excess of 1 percent often result. Hence the authors highly recommend that in work where transmissions are desired, as in the case of ozone studies, perforated metal screens having approximately the same transmissions as the glass filters be employed as incorporated in the stratosphere ultraviolet meter at the National Bureau of Standards (**5, 13**). An addition that would be necessary with the use of perforated screens is a quartz diffusing window over the photoelectric cell. This would reduce variations in reading as the angle of the solar adjustment changed during a set of measurements. Furthermore, since the magnitude of the readings, filter and screen, would be of the same order, both could be kept near the upper end of the scale thereby reducing the scale error in reading. Even more important than this would be the reduction of error due to zero shift and setting of the instrument which would be largely automatically compensated for by having the readings of similar magnitude.

It is along these lines that it is hoped to attain, in subsequent work, sufficient accuracy with an automatically recording instrument now under construction.

IV. THE METHOD FOR EVALUATING THE AMOUNT OF OZONE

Using four filters, measurements were made with two titanium photoelectric cells in July 1936, and with two other cells in July 1938. The transmissions in percent for the different filters, are plotted as a function of the solar air mass at the time of the observations.

In order to obtain a measure of the amount of ozone at the time of the observations, two methods have been employed. By the first method a solar energy curve outside the atmosphere is assumed. For this, observational data obtained by Pettit (**6**) is used (see fig. 9). Starting with this spectral energy curve, and by a process of integration (using 20 angstroms as a unit) a set of transmission curves for three of the filters having total transmissions of approximately 15, 40, and 60 percent for one of the photoelectric cells, as a function of solar air mass has been calculated. For these calculations the Fabry and Buisson (**7**) transmission coefficients for ozone and the Rayleigh scattering (atmospheric transmission) coefficients as used by O'Brien (**8**) in the reduction of the stratosphere balloon data (Explorer I and II) have been used. Some of the ozone and scattering transmission curves which were employed are reproduced in figure 4.

While this method gives values which are roughly in agreement with those obtained as described below, the calculated values indicate less ozone for the noon observations and more for the morning and afternoon (high air mass) measurements (see fig. 5). Hence the Pettit curve does not appear to be sufficiently accurate for this purpose, in that it is too low in value for the shorter wavelengths. The authors have therefore by the second method, similar to that employed by Stair and Coblentz in their stratosphere work, (**2**) set up a solar energy curve—not outside the atmosphere but within the range of air masses covered by the observations. First, by a method previously used by Coblentz and Stair (**3**) an approximate solar energy curve is set up for an air mass near the noon hour (low air mass), and adjusted until the calculated integral transmissions of the filters are in agreement with the observed values for some particular low air mass. Then, having a spectral solar energy curve which gives calculated transmissions for a photoelectric cell (No. 2 in this case) in agreement with the observations for one air mass, m= 1.06, for example (see fig. 5), calculations are made for transmissions at other air masses covering the air mass range of observations, for different amounts of ozone. This gives a diverging set of curves (A, B, and C, in fig. 5)

[5] Incidentally the device makes an excellent instrument around the laboratory for measuring extremely high resistances (low leakages) and small capacitances.

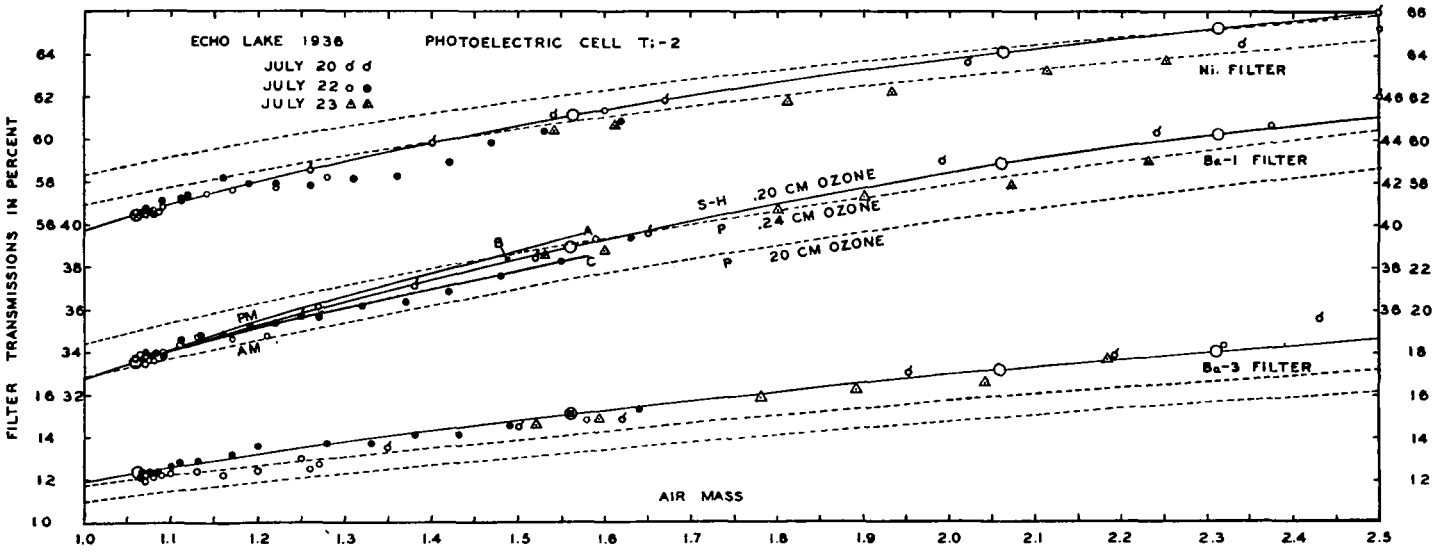

FIGURE 5.—Graphs showing the amount of ozone in the stratosphere, based on observations with titanium photoelectric cell No. 2; P, calculations based on the Pettit curve for air mass, m=0; S=H, calculations based on Stair-Hand solar energy curve, m=0, as determined from the observations for the two mornings, July 20 and 22, 1936.

through the value for air mass 1.06. The curve best representative of the observed data defines the amount of ozone above the observer at the time. In this case curve B for 0.20 cm. of ozone represents the data for the two mornings July 20 and 22. Curve C might have been chosen and the data for the afternoon of July 22 employed, yet this would be a bad choice since there are definite indications that the ozone value was changing.

The method is best presented by giving an example. Table 1 illustrates the calculations and method for obtaining one point (at air mass 1.56, see fig. 5) in one of the diverging curves for each of the three filters (Ni, Ba–1, Ba–3) through the point for air mass 1.06 referred to in the above example for titanium cell No. 2. In this table, column 1 gives the center of the wave-length interval and column 2 the relative spectral energy values found previously to give calculated transmissions of the filters which agree with the observed values for air mass 1.06. In column 3 are given transmission values for air mass 0.5 when scattering only is taken into account, since this calculation is to apply to air mass 1.56 and the starting values are already incorporated for m=1.06. Similarly transmission values for 0.10 cm. ozone—the ozone content of air mass 0.5—are used (given in column 4) because in the present illustration the diverging curve for 0.20 cm. of ozone is being calculated.

The product of columns 2, 3, and 4 gives column 5 which represents, therefore, a solar energy curve for air mass 1.56 and 0.20 cm. ozone. In column 6 the relative spectral response values (for equal energy) for photoelectric cell No. 2 are tabulated. The product (column 7) of columns 5 and 6 gives, consequently, the calculated integral response of the photoelectric cell for solar radiation, air mass 1.56, ozone value 0.20 cm. Columns 8, 10, and

TABLE 1.—*Illustrating the method employed in the calculation of ozone values*

Center of wave-length interval A	Relative energy M = 1.06	Scattering transmission M = 0.5	Transmission 0.10 cm. ozone	Columns 2 × 3 × 4 relative energy M=1.56	Relative response Ti-2	Columns 5 × 6 integrated response	Transmission Ni	Columns 7 × 8 integrated response	Transmission Ba-1	Columns 7 × 10 integrated response	Transmission Ba-3	Columns 7 × 12 integrated response
1	2	3	4	5	6	7	8	9	10	11	12	13
2900		0.646	0.010		0.76		0.014					
2920		.653	.033		.76		.039					
2940		.660	.077		.75		.070					
2960	0.3	.667	.140	0.03	.73	0.02	.100					
2980	.9	.674	.240	.15	.70	.10	.132	0.01				
3,000	1.75	.681	.325	.39	.66	.26	.165	.04				
3,020	2.6	.688	.415	.74	.62	.46	.204	.09	0.003			
3,040	3.55	.694	.500	1.23	.58	.71	.246	.18	.017	0.01		
3,060	4.65	.700	.580	1.89	.53	1.00	.293	.29	.035	.04		
3,080	6.2	.707	.660	2.89	.49	1.42	.343	.49	.060	.09		
3,100	7.2	.713	.725	3.72	.45	1.67	.398	.67	.090	.15		
3,120	8.6	.719	.780	4.82	.405	1.95	.457	.89	.133	.26	0.001	
3,140	10.1	.725	.825	6.04	.36	2.17	.514	1.12	.180	.39	.008	0.02
3,160	11.3	.731	.865	7.14	.32	2.29	.563	1.29	.237	.54	.023	.05
3,180	13.5	.737	.900	8.95	.285	2.55	.605	1.54	.310	.79	.042	.11
3,200	16.5	.744	.925	11.36	.245	2.78	.645	1.79	.380	1.06	.075	.21
3,220	21.2	.750	.943	14.99	.210	3.15	.680	2.14	.455	1.43	.127	.40
3,240	26.0	.756	.955	18.77	.175	3.29	.710	2.33	.526	1.73	.190	.62
3,260	30.2	.762	.966	22.23	.14	3.11	.737	2.29	.58	1.80	.25	.78
3,280	34.4	.768	.974	25.74	.105	2.70	.757	2.05	.63	1.70	.315	.85
3,300	38.9	.773	.982	29.53	.075	2.21	.775	1.72	.67	1.48	.38	.84
3,320	42	.779	.986	32.25	.045	1.42	.792	1.12	.703	1.00	.44	.62
3,340	45	.784	.989	34.9	.023	.80	.805	.65	.736	.59	.505	.41
3,360	48	.790	.993	37.6	.010	.38	.818	.31	.766	.29	.555	.21
3,380	50	.796	.997	39.7	.003	.12	.829	.10	.79	.09	.60	.07
Total						34.56		21.11		13.44		5.19
Percentage transmission								61.1		38.9		15.0

12 give the spectral transmissions of the three filters and columns 9, 11, and 13 the integrated photoelectric response through the three filters respectively. From the sums of the integrated values for the photoelectric cell alone and through the several filters the calculated filter percentage transmissions are obtained directly as ratios—e. g. 21.11÷34.56=61.1 percent. In this particular case the three values are 61.1, 38.9, and 15.0 percent and are plotted as large circles in figure 5 at air mass 1.56. Other points on the same curves and on other curves for differing amounts of ozone are similarly calculated.

Having determined the amount of ozone for a particular day, and using the solar energy curve in agreement with the observed data for one air mass (m=1.06 for the data of fig. 5), it is a simple matter, by a calculation which is the reverse of that illustrated in table 1, to calculate the relative solar energy curve for sunlight outside the atmosphere; and then from it transmission values for other amounts of ozone, other than the value in agreement with the data for that particular day, or days. This gives a set of nearly parallel curves (see figs. 6, 7, and 8), from which may be read the amount of ozone corresponding to any observed filter transmission when plotted as a function of

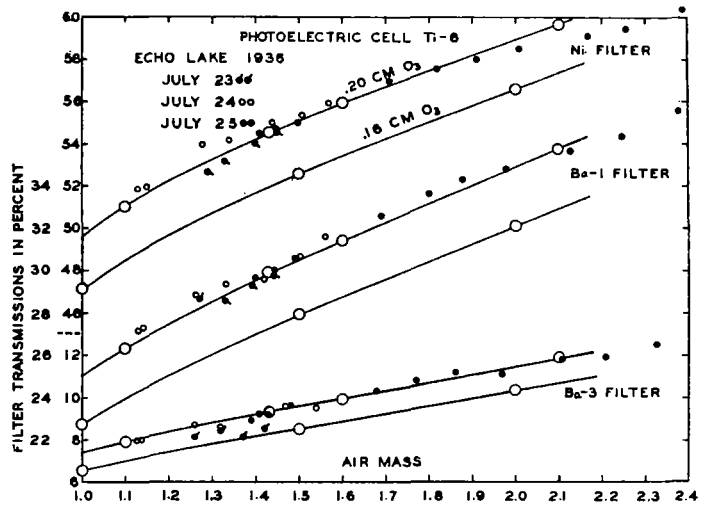

FIGURE 6.—Graphs showing the amount of ozone in the stratosphere, based on the observations with titanium photoelectric cell No. 6.

air mass. Although the preliminary calibrations and calculations for a particular photoelectric cell and set of filters are quite complicated, when these are once made it is simple from this set of curves to determine the ozone value from measurements with a single filter within a few minutes time. This is a highly important factor should such measurements become useful for forecasting purposes.

V. AMOUNT OF OZONE OVER MOUNT EVANS

In figures 5, 6, 7, and 8 are represented the observed data and the calculated amounts of ozone above Mount Evans as determined with the four photoelectric cells for the days on which measurements were obtained. While the data show much irregularity, which may in part be credited to instrumental difficulty, there are certain variations especially on July 22, 1936 (see fig. 5) when the ozone value was quite constant at 0.20 cm. (normal temperature and pressure) from early morning until 2:00 p. m., when it suddenly decreased to about 0.18 cm., or slightly less by 3:00 p. m., and then increased again to about 0.19 cm. by 4:00 p. m. The upper air mass maps for this date indicate a change in air mass, presumably at about the time that the

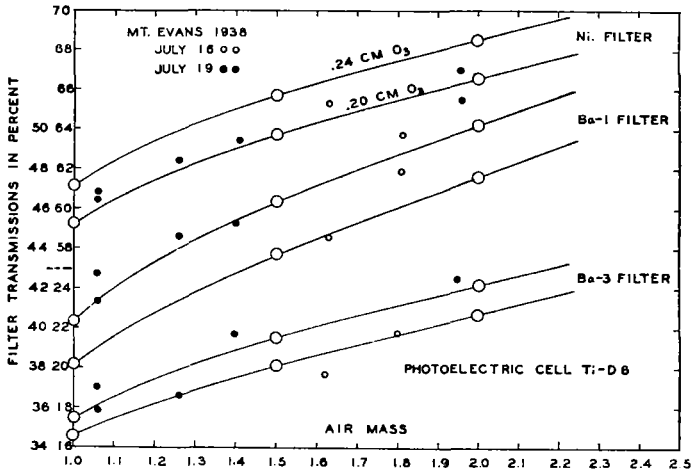

FIGURE 7.—Graphs showing the amount of ozone in the stratosphere, based on the observations with titanium photoelectric cell D–6.

ozone content changed.[6] On July 20 and July 23, 1936 our measurements and calculations indicate a fairly constant amount of ozone at about 0.20 cm. and 0.18 cm. respectively.

On July 23, 24, and 25, 1936, as measured with photoelectric cell No. 6 the value of ozone appeared to fluctuate around the 0.20 cm. value (see fig. 6) being possibly slightly lower on July 23, in agreement with data obtained earlier in the day with cell No. 2 (see fig. 5) and higher on July 24.

On July 16 and 19, 1938 (see fig. 7) the filter transmissions obtained by photoelectric cell D–6 indicate ozone in the amount of about 0.22 cm. normal temperature and pressure. July 19 was clear from early morning until noon. Two sets of measurements made near the noon

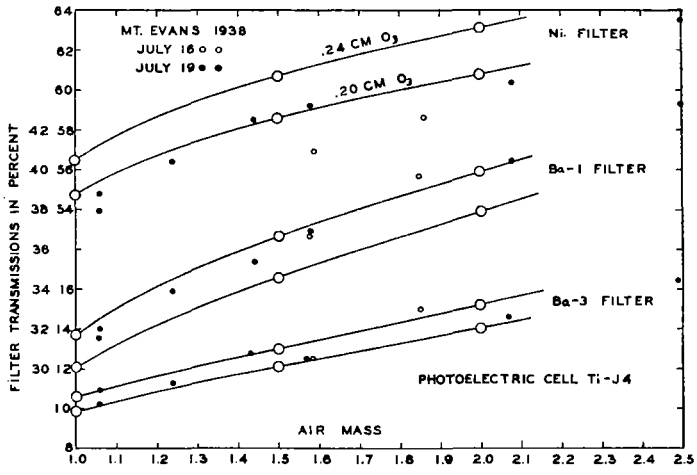

FIGURE 8.—Graphs showing the amount of ozone in the stratosphere, based on the observations with titanium photoelectric cell J–4.

hour, air mass 1.06, showed rapidly increasing transmissions for all the filters indicating an increase in ozone value of about 0.02 cm. within a period of less than an hour.

Alternate measurements were made on the same 2 days with cell J–4. The calculated amount of ozone based upon measurements with this cell was about 0.22 cm. in agreement with that for cell D–6 (see fig. 8). Considering the difficulties involved this agreement is remarkable, in view of the limited observations. Furthermore, the same increase of about 0.02 cm. ozone is to be noted in the noon measurements (air mass 1.06) with this cell.

[6] No correction has been made for possible temperature changes within the ozone layer

In connection with the change in ozone content on July 16 and 19, 1938, after inspection of the surface, upper air and isentropic charts, P. J. Harney of the Air Mass section of the Weather Bureau concludes:

> On both July 16 and 19 surface cold fronts passed on the east side of the mountains from the north and I would say there was a change of air mass at your station (Mount Evans) also. The following air was a few degrees cooler and had a 10 percent higher relative humidity on the Cheyenne APOB (airplane observation) at about 16,000 feet elevation on each day. However at your station we are not certain but that the air may have been in another air mass than that which was shown at Cheyenne with a change in it to be expected simultaneously with the change in the surface trough mentioned above. The upper winds indicate that the air arriving during July 16 came from the west and on the 19th from the northeast but both air masses were probably of Pacific origin.

To date the paucity of the available data prevents any definite conclusions as to the relation between changes in ozone content and change in type of air although in every case where the observations have shown a definite change in ozone content, there also has been an apparent change in the origin of the air.

VI. THE SOLAR ENERGY CURVE OUTSIDE THE ATMOSPHERE

It is to be noted that the relative solar energy curve outside the atmosphere [7] was calculated independently for each of the four cells. While the results obtained are not in exact agreement, the mean of the four determinations gives a relative energy curve which appears to be near the correct value in the spectral range 3,000 to 3,250 A. (see fig. 9).

By the same method as previously employed by Coblentz and Stair **(3)** for the reduction of their ultraviolet measurements to absolute value, for wavelengths 3,132 and shorter, we have evaluated our relative energy curve outside the atmosphere to yield absolute units, and for comparison this curve (average obtained for our four cells) is given along with an average for Petitt's data **(6)** at Mount Wilson and that of Coblentz and Stair **(11)** at Washington, D. C.

As may be seen from the figure our solar energy curve for m=0 is in close agreement with the others between 3,100 and 3,250 angstroms. Below 3,100 A. our curve indicates higher energy values in the form of a maximum at about 3,000 A. This is in agreement with some unpublished data of Brian O'Brien presented at a meeting of the Philosophical Society in Washington on May 20, 1939.

Incidently the curve calculated using the data obtained with photoelectric cell D–6 (fig. 9) coincides exactly with the average curve throughout the range 3000 to 3,250 A. in both shape and energy value. The calculated curves using cells Nos. 2 and 6 were in close agreement in general shape, but differed 5 to 20 percent in absolute energy values. This fact was unimportant in ozone calculations since only the shape of the curve, and not energy values, enter into the calculations. The calculations for cell J–4 differed most from the average. Energy values from 3,100 to 3,250 A. were in close agreement with those obtained with the other cells but below 3,100 A. a lower value was calculated. This is the least sensitive of the four cells and responds to a shorter spectral band. A small sensitivity to longer wave lengths not detected might account for this difference.

It is a distinct advantage to use several photoelectric cells with different spectral ranges to obtain more precise values of the spectral solar energy curve. However, once the solar energy curve is accurately determined within the region of these short wavelengths future work will be greatly simplified and it will be more efficient to use only one, or at most two filters, having a total integrated transmission near 50 percent, since the transmission of a filter in that range is most sensitive to ozone changes when used with a photoelectric cell of the type employed in this work.

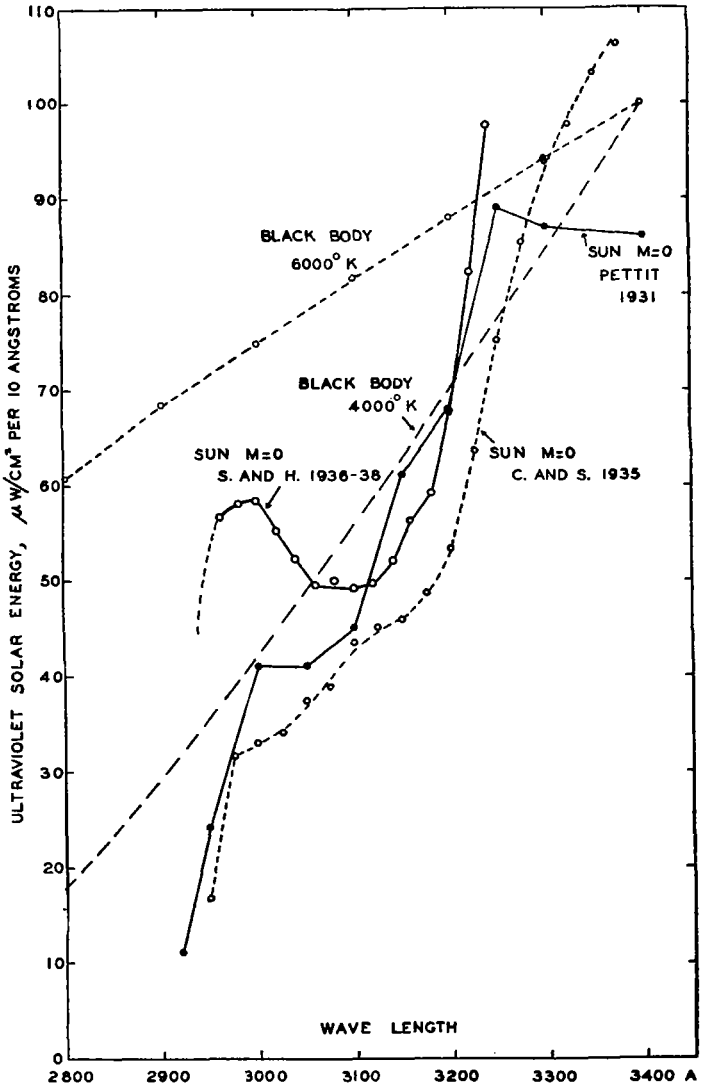

FIGURE 9.—Distribution of energy in the extreme ultraviolet of the solar spectrum. The S and H (Stair and Hand) curve is the average of the four determinations at Mount Evans with the four photoelectric cells. Curves by other observers and for a black body are given for comparative purposes.

VII. CONCLUSIONS

While the data herein discussed are not extensive nor are the calibrations of the photoelectric cells in absolute agreement, the method promises an accurate measure of the ozone in the stratosphere. The preliminary calibrations and calculations for a particular photoelectric cell and set of filters is complicated, but when these are once made it should be possible, from a set of curves, to determine the ozone value from measurements with a single filter within a few minutes. This is a highly important factor should such measurements be used for forecasting purposes. In practice it may often be much more satisfactory to calibrate a complete new instrument

[7] The present and previous authors working in this field, are of course cognizant of the fact that the real spectral energy curve of solar radiation is not smooth but is indented by many absorption lines.

by comparison with a calibrated one rather than to go back to absolute units of microwatts, angstroms, etc., as we have purposely done in the present case for each photoelectric cell.

The values for the amount of ozone above Mount Evans as determined by the four cells are in close agreement. Two of the cells indicated a value of about 0.20 cm. normal temperature and pressure, while the other two cells indicated about 0.22 cm. This is in close agreement with that of other observers (**1, 9**) for the same latitude and season of the year.

In conclusion, we wish to express our appreciation to W. W. Coblentz of the National Bureau of Standards, and to J. C. Stearns of the University of Denver, for helpful assistance, especially in arranging for the work, and for making available the use of Mount Evans Observatory. We wish also to express our thanks to K. W. Kemper of the Lincoln, Nebr., Weather office, who, at his own expense, assisted in the observational program on the top of Mount Evans.

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VARIATION IN SOLAR RADIATION INTENSITIES AT THE SURFACE OF THE EARTH IN THE UNITED STATES

By IRVING F. HAND

[Weather Bureau, Washington, D. C., May 1939]

This paper brings up to date two articles on the same subject published by Kimball in 1918 (**1**) and 1924 (**2**); however, the data here given are from stations in the United States only, whereas the previous papers included all available data for the entire globe.

The departures from normal were obtained by averaging the mean departures of each month's means for the three Weather Bureau radiation stations at Washington, D. C., Madison, Wis., and Lincoln, Nebr., and also for the Blue Hill station of Harvard University for the few years that this station has been in operation, and finally smoothing out the departures by the formula $(a+2b+c)/4$, where b is the average percentage departure for the month in question, and a and c are the average percentage departures for the preceding and following months, respectively. The smoothed percentages have been plotted in figure 1, and the same data tabulated in table 1.

Owing to the small number of stations, local influences, such as duststorms, forest fires, irregular manufacturing activity, etc., are important factors in the fluctuations shown by the curve.

Although three major and several minor volcanic eruptions occurred during this 15-year period, no conclusive evidence appears that any of them depleted the solar energy received at the surface of the earth in the United States. The most violent explosive eruption during this period took place on the Isle Flores, Dutch East Indies, latitude 8° S. in August and September 1928, when an estimated 19½ million cubic meters of material were emitted. About the same amount of material was discharged from Quisapu volcano in Chile during its eruption in April 1929, but the proportion of lava-flow from this latter volcano was much greater than from the East Indies eruption. Although apparently neither eruption appreciably affected radiation receipt in the United States, it is interesting to note that the 1 or 2 months immediately following each explosion were those of minimum radiation receipt for the respective years. It is quite evident neither eruption carried large quantities of dust into the stratosphere; and in the case of the Chilean eruption we would expect very little dust to be transported across the equator from so southerly a latitude. The third violent eruption during the period occurred on the isle of Martinique in 1929 when Mount Pelée once again altered its skyline, this time without serious damage. That this eruption had little effect upon solar receipt is evident from the fact that solar radiation intensities began to increase immediately following the time of the volcanic activity.

As a matter of comparison with previous periods when volcanic activity did affect very appreciably solar radiation receipt at the earth's surface, we review briefly the effect of Krakatoa, Malay East Indies, latitude 7° S.; the explosion carried away the top of that mountain with such a detonation that it was heard for hundreds of miles, and with an emission of dust sufficient to deplete solar radiation receipt to but 84 percent of its normal. In 1902 the eruptions of Pelée on the island of Martinique, Santa Maria in Guatemala, and Colima in Mexico were followed almost immediately by an 18 percent diminution in intensity of radiation. The eruption of Katmai in Alaska on June 6, 1912, threw a tremendous amount of volcanic ash into the stratosphere which resulted in a decrease of 22 percent in radiation receipt, and a continuation of gradually lessening atmospheric contamination for 2 years.

In all three cases, owing to decreased solar heating of the earth, temperatures remained subnormal for at least a year following the individual explosions. With this in mind, attention may be drawn to the fact that temperatures in this country have been considerably above normal during the past 8 years, although this condition may have no relation to the increased radiation receipt.

The lack of volcanic eruptions of the type that throws dust into the stratosphere accounts for the general increase in radiation during the period 1924–38. It is far more difficult to explain why individual years show such a marked increase in radiation. However, there seems to